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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09B 62/09

A1

(11) International Publication Number: WO 98/20077

(43) International Publication Date: 14 May 1998 (14.05.98)

(21) International Application Number: PCT/IB97/01372

(22) International Filing Date: 31 October 1997 (31.10.97)

(30) Priority Data:
9622912.5 4 November 1996 (04.11.96) GB

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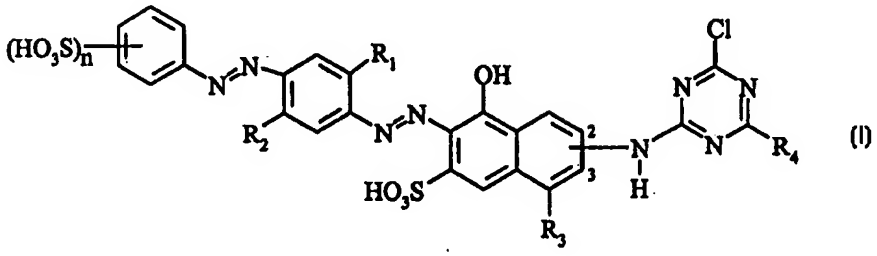
(81) Designated States: BR, CN, ID, JP, MX, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: DISAZO REACTIVE DYESTUFFS



(I)

(57) Abstract

A fiber-reactive dyestuff having formula (I) or a salt thereof wherein the significances of the substituents are herein defined. The fiber-reactive dyestuff has good fixation properties and produces dyeings and prints with good light and wet fastness properties.

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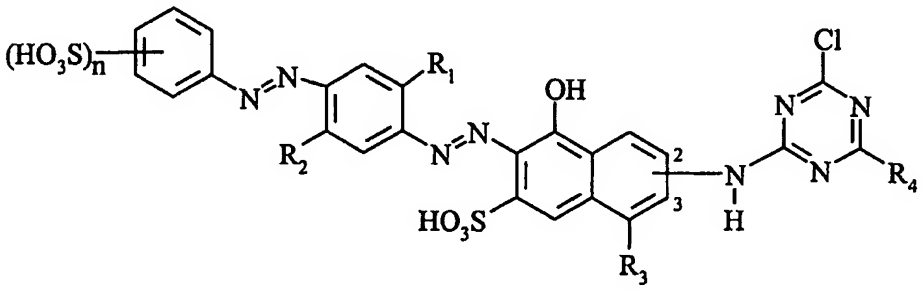
DISAZO REACTIVE DYESTUFFS

This invention relates to fiber-reactive dyestuffs, in particular disazo fiber-reactive dyestuffs bearing a chlorotriazinyl reactive group.

The invention provides in one of its aspects a fiber-reactive dyestuff having the formula (I) or a salt thereof



(I)

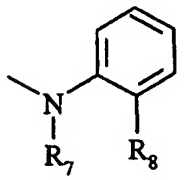
wherein

R_1 is H or $-SO_3H$, preferably $-SO_3H$;

R_2 is H, methyl, $-NHCONH_2$ or $-NHCOCH_3$, preferably hydrogen;

R_3 is H or $-SO_3H$, preferably hydrogen;

R_4 is $-NR_5R_6$ wherein R_5 and R_6 are independently selected from H, C_{1-4} alkyl, preferably methyl or ethyl, optionally substituted with CN, OH, Cl, F or $-SO_3H$; or R_5 and R_6 together with the nitrogen atom form a 5 or 6 membered ring optionally containing a nitrogen or oxygen atom, e.g. morpholino; or R_4 is a radical of the formula (ii)



(ii)

preferably R_4 is a radical of the formula (ii)

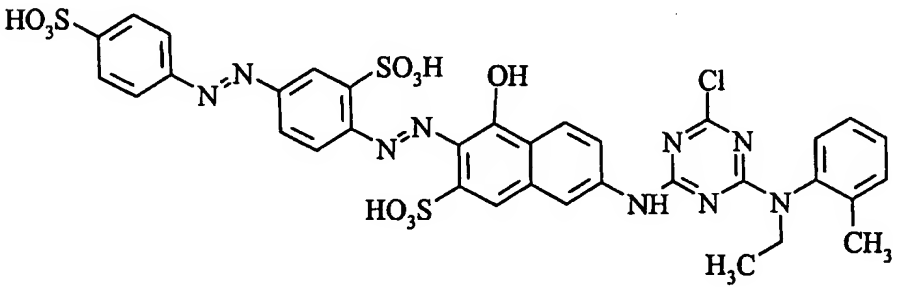
wherein

R_7 is H, C_{1-4} alkyl, preferably methyl or ethyl, optionally substituted with CN, OH, Cl, F or $-SO_3H$, preferably ethyl, and

R_8 is H, halogen, e.g. F, Cl or Br, C_{1-4} alkyl or C_{1-4} alkoxy, preferably methyl, and

n is 1 or 2.

In a preferred aspect of the invention there is provided a fiber-reactive dyestuff according to the formula (iii)



(iii)

or a salt thereof.

When the compounds of formula (I) are in the salt form the constitution of the cation is not important and may be any of the non-chromophoric cations conventional in the chemistry of fiber-reactive dyestuff chemistry provided that the corresponding salt fulfills the requirement of water solubility. Examples of suitable cations are alkali metal cations or substituted or unsubstituted ammonium ions, for example lithium, sodium, ammonium, mono- di- and tri-ethanolammonium cations. Preferred cations are the alkali metal cations and the ammonium cation of which the sodium cation is particularly preferred.

The cations associated with the compound in its salt-form may be the same or different, that is, the compound may be produced in a mixed salt-form.

The invention provides in another of its aspects a process of forming a fiber-reactive dyestuff hereinabove described.

The fiber-reactive dyestuff may be formed when a chlorotriazinyl group precursor is reacted with an amino group having a reactive hydrogen atom which amino-group is connected to a

disazo-dyestuff or a disazo-dyestuff intermediate according to a conventional synthesis. In a preferred process, the chlorotriazinyl group precursor is connected to a disazo-dyestuff intermediate, e.g. 2-amino-5-hydroxynaphthalene-7-sulphonic acid and coupling the fiber-reactive dyestuff intermediate so formed with a diazotised amine of an appropriately substituted azo-benzene.

When the chlorotriazinyl group precursor does not contain a substituent R_4, this substituent can be attached to the fiber-reactive triazinyl group after the fiber-reactive dyestuff has been formed by reacting a labile halogen atom, e.g. Cl on the fiber-reactive triazinyl radical with the appropriate amine, e.g. N-ethyl -o- toluidine according to a conventional synthesis.

The coupling reaction hereinabove mentioned is preferably carried out in an aqueous medium at a temperature of from 0 to 5°C and under acidic conditions, e.g. pH 1 to 2.

The substitution reaction whereby a fiber-reactive triazinyl group precursor is reacted with a disazo-dyestuff or a disazo-dyestuff intermediate may be conveniently carried out in an aqueous medium at a temperature of from 0 to 5°C and under acidic conditions, e.g. pH 2 to 3 for a period of about 1 hour.

The reaction of a fiber-reactive triazinyl group precursor with an appropriate amine is conveniently carried out in an aqueous medium at a temperature of from 50 to 60°C and a neutral to slightly basic pH, e.g. 7 to 8.

Isolation of the fiber-reactive dyestuff may take place according to known techniques, e.g. the fiber-reactive dyestuff may be separated from the reaction mixture by salting-out with alkali metal salts before filtering and drying optionally at elevated temperature and under vacuum.

Depending upon the reaction and isolation conditions, a fiber-reactive dyestuff of formula (I) will be obtained as a free acid or in the salt-form. The salt-form can be transformed into the free acid and vice versa according to known techniques.

A fiber-reactive dyestuff of the invention is suitable for dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates. Preferred substrates include leather and

fibrous substrates which consist of or contain natural or synthetic polyamides and in particular natural or regenerated cellulose, such as cotton, viscose or rayon staple fiber.

A fiber-reactive dyestuff of formula (I) or a salt thereof may be employed in dyebaths or in printing pastes according to all the dyeing and printing processes which are conventional for reactive dyes. Dyeing is preferably carried out using the exhaust process at a temperature of from 80 to 100°C.

The fiber-reactive dyestuffs of formula (I) or a salt thereof may be used as an individual dyestuff in a dyebath or, in view of its good compatibility with certain other reactive dyestuffs, in a dyeing composition with appropriate other reactive dyes of the same class, that is, other dyestuffs which display comparable dyeing properties, e.g. fastness properties and exhaust values.

The fiber-reactive dyestuffs of formula (I) display good fixation values. Dyeings and prints exhibit good fastness properties, e.g. light and wet fastness and fastness to oxidative influences such as chlorine-containing water, perborate detergents, hypochlorite bleaches and peroxide bleaches. Especially their light fastness is unexpectedly high.

The following examples serve to illustrate the invention.

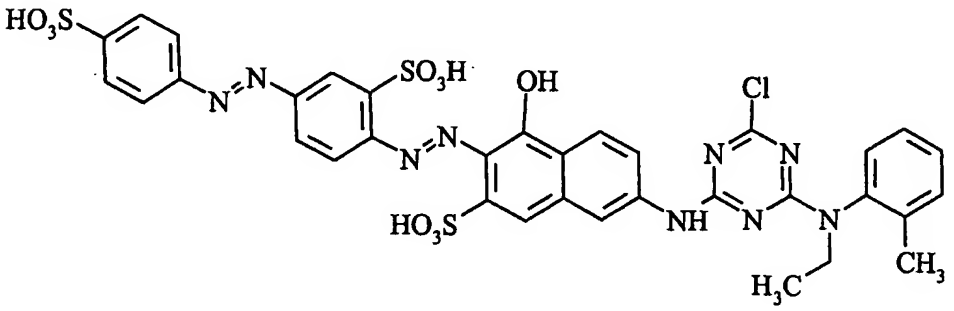
EXAMPLE 1

36.9 Parts of 2,4,6-trichlorotriazine are stirred into 300 parts of water at 0-5°C. To this suspension is added a suspension of 47.8 parts of 2-amino-5-hydroxynaphthalene-7-sulfonic acid over a 60 minutes period. At the same time a 20 % solution of sodium carbonate is added to this mixture continuously in order to maintain the pH of the mixture at 2-3. The end point of the reaction is determined using chromatographic techniques.

The resultant suspension is allowed to adjust to room temperature before being poured onto a diazonium salt solution which is formed of 71.5 parts of 4-amino-1,1'-azobenzene-3,4'-disulfonic acid and 50 parts by volume of 4N sodium nitrite solution at 0-5°C and a pH of 1. The resultant coupling reaction mixture is maintained at a pH of 7-8 by continuously adding 20 % sodium carbonate solution. After the reaction is complete 29.7 parts of N-ethyl-o-

toluidine are added and the reaction mixture heated to 50-60°C. At the same time a 20 % of sodium carbonate solution is added to this mixture continuously in order to maintain the pH of the mixture at 7-8.

The disazo compound thus formed is salted-out using conventional methods, filtered and dried at 50°C under vacuum. The product has the formula



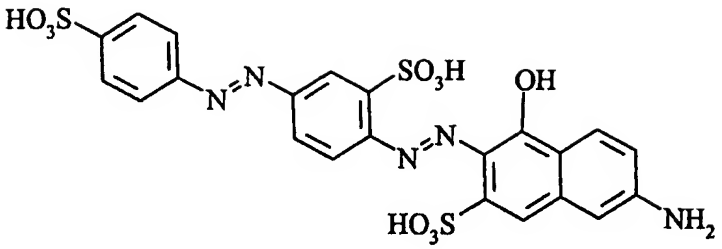
λ max 513 nm in H_2O

This product dyes cotton to a red shade. The resultant dyeing displays excellent light and wet fastness properties and is resistant towards oxidative influences.

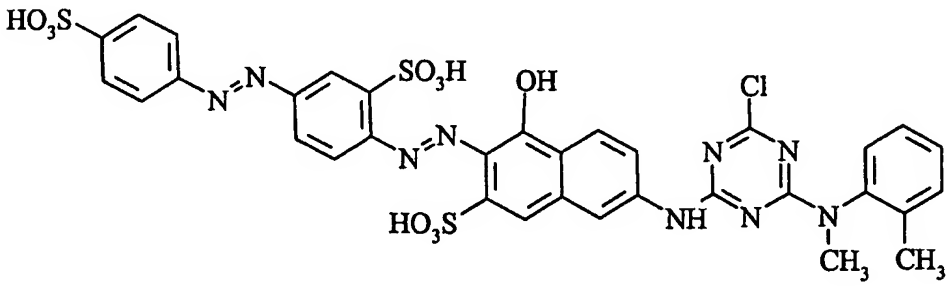
EXAMPLE 2

A solution of 28.1 parts of 2-acetylamino-5-hydroxynaphthalene-7-sulfonic acid in 200 parts of water at 25°C are mixed with a diazonium salt solution formed at 0-5°C and a pH of 1 from a mixture of 35.8 parts of 4-amino-1,1'-azobenzene-3,4'-disulfonic acid and 25 parts by volume of 4N sodium nitrite solution.

The resultant coupling reaction mixture is maintained at a pH of 7-8 by the continuous addition of a 20 % sodium carbonate solution. At the end of the reaction the product obtained is salted-out using conventional methods, filtered and dried by suction. The still damp residue after suction filtration is dissolved in 300 parts of 4 % by weight solution of sodium hydroxide and the resultant solution is heated to 90-100°C until saponification of the acetyl group is complete as determined by thin layer chromatography. The solution of the compound thus obtained having the formula



is cooled to room temperature and by adding 30 % hydrochloric acid the pH is adjusted to 6. At this pH 18.5 parts of 2,4,6-trichlorotriazine are added in portions over a 15 minutes period and stirred for 120 minutes. The pH of the reaction mixture is maintained by the continuous addition of 20 % sodium carbonate solution at 6-6.5. Upon completion of reaction 13.3 parts of N-methylamino-2-methylbenzene is added and the mixture is heated to 50-55°C maintaining the pH by the continuous addition of 20 % sodium carbonate solution at 6-6.5. At the end of condensation the resultant dyestuff is salted-out by conventional methods, filtered by suction and dried at 50°C under vacuum. The product having the formula



λ max 512 nm in H_2O

dyes and prints cotton to a red shade. Dyeing and prints thus obtained display excellent light and wet fastness properties and are stable to oxidative influences.

EXAMPLES 3-13

Table 1 discloses several dyestuffs which are formed according to methods analogous to those described in Examples 1 and 2 and employing corresponding starting materials. In all cases the dyestuffs obtained dye cotton to a red shade and dyeings thus obtained display excellent light and wet fastness and are stable to oxidative influences.

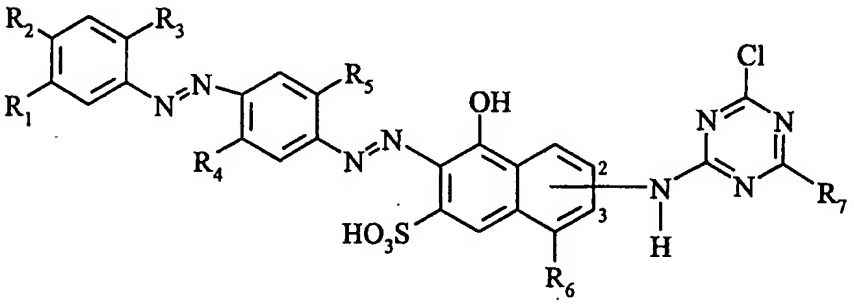
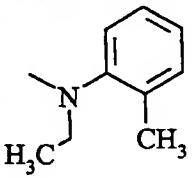
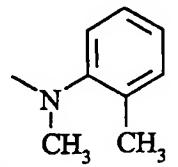
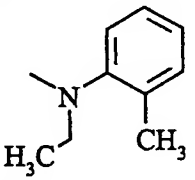
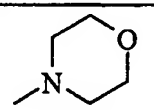
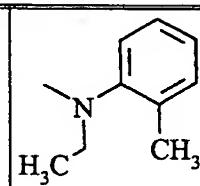


TABLE 1

Ex.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Pos. -NH-	λmax nm in H_2O
3	H	SO_3H	H	H	SO_3H	H		2	532
4	H	SO_3H	H	H	SO_3H	H		2	531
5	H	SO_3H	H	H	SO_3H	SO_3H		3	510
6	H	SO_3H	H	H	SO_3H	H		3	514
7	H	SO_3H	H	H	SO_3H	H	do.	2	533
8	H	SO_3H	H	H	SO_3H	H	$-NHCH_2CH_2OH$	3	513

9	H	SO_3H	H	H	H	SO_3H		3	518
10	SO_3H	H	SO_3H	$-NHCONH_2$	H	H	do.	3	520
11	H	SO_3H	SO_3H	Me	H	SO_3H	do.	3	519
12	H	SO_3H	H	H	SO_3H	H	$-NH_2$	3	511
13	H	SO_3H	H	H	SO_3H	H	$-NH_2$	2	530

APPLICATION EXAMPLE A

A dyebath consisting of 1000 parts of demineralised water, 80 parts of Glauber's salt (calcined), 1 part of the sodium salt of 1-nitrobenzene-3-sulphonic acid and 1 part of the fiber-reactive dyestuff of Example 1 were heated to 80°C over the course of 10 minutes. Thereafter, 100 parts of mercerized cotton are immersed in the resultant solution. Dyeing is effected at 80°C over a period of 5 minutes before the solution is raised to a temperature of 95°C over a period of 15 minutes. After 10 minutes at 95°C, 3 parts of soda are added followed by a further 7 parts of soda after 20 minutes and another 10 parts of soda after 30 minutes. Dyeing is subsequently continued for a further 60 minutes at 95°C. The dyed material is then removed from the dyebath, rinsed for 2 minutes under demineralised water at 60°C plus or minus 10°C and for a further 1 minute under running water at the same temperature. Thereafter the material is washed twice for 10 minutes, each time in 5000 parts of boiling demineralised water, and subsequently rinsed for 2 minutes under running demineralised water at 60°C plus or minus 10°C and 1 minute under running tap water at the same temperature. After drying, a brilliant red color cotton dyeing with good fastness is obtained.

APPLICATION EXAMPLE B

A printing paste having the following components

40	parts of the fiber-reactive dyestuff of Example 1
100	parts of urea
330	parts of water
500	parts of a 4% sodium alginate thickener
10	parts of the sodium salt of 1-nitrobenzene-3-sulphonic acid
20	parts of soda
1000	parts in total

is applied to cotton material by conventional printing processes.

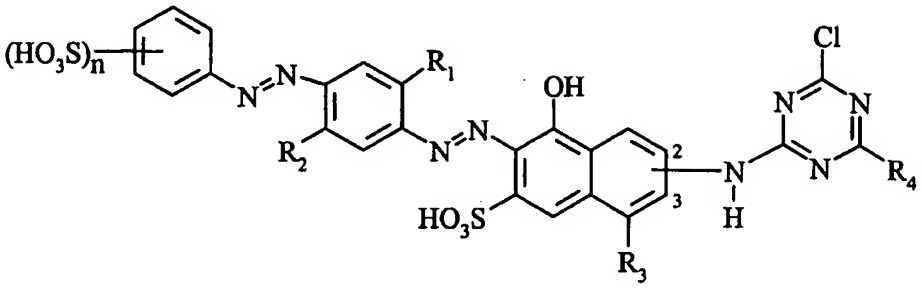
The printed and dried material is steamed for 4 to 8 hours at 102 to 105°C before being given a cold and a hot rinse. The fixed cotton material was subsequently washed at the boil

(analogously to Example A) and dried. A red colored print is obtained having good fastness properties.

The fiber-reactive dyestuffs of Examples 2 to 13 are also used for dyeing and printing according to the processes described in Application Examples A and B.

CLAIMS

1. A fiber-reactive dyestuff of formula (I)



(I)

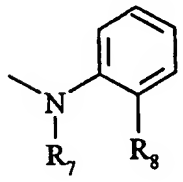
wherein

R_1 is H or $-SO_3H$;

R_2 is H, methyl, $-NHCONH_2$ or $-NHCOCH_3$;

R_3 is H or $-SO_3H$;

R_4 is $-NR_5R_6$ wherein R_5 and R_6 are independently selected from H, C_{1-4} alkyl, optionally substituted with CN, OH, Cl, F or $-SO_3H$; or R_5 and R_6 together with the nitrogen atom form a 5 or 6 membered ring optionally containing a nitrogen or oxygen atom; or R_4 is a radical of the formula (ii)



(ii)

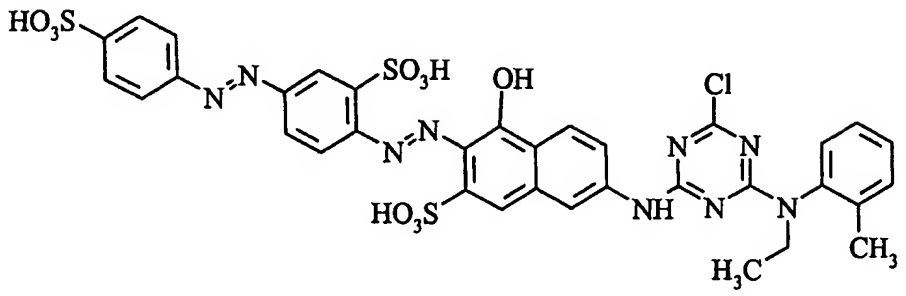
wherein

R_7 is H, C_{1-4} alkyl, optionally substituted with CN, OH, Cl, F or $-SO_3H$;

R_8 is H, halogen, C_{1-4} alkyl or C_{1-4} alkoxy, and

n is 1 or 2.

2. A fiber-reactive dyestuff according to formula I of the formula (iii)



(iii)

or a salt thereof.

3. A process of forming a fiber-reactive dyestuff of formula (I) as defined in Claim 1 comprising the step of reacting the appropriately substituted disazo-dyestuff containing a di-chlorotriazinyl group with an amine R_4-H.

4. A process of dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates comprising the use of a fiber-reactive dyestuff according to formula I as defined in claim 1.

5. Hydroxy-group-containing and nitrogen-containing organic substrates which have been dyed or printed in accordance with the process of claim 4.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/01372

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B62/09

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 254 335 A (SANDOZ LTD) 7 October 1992 see claim 1; examples 7,26	1,3-5
X	WO 95 21892 A (ZENECA LTD ;TAYLOR JOHN ANTHONY (GB)) 17 August 1995 see example 1, stage a)-stage c); examples 3,7,9,10,12,13,15,16,25-31,34,45-50,52	1,3-5
X	FR 1 180 920 A (CIBA) 10 June 1959 see example 25	1,3-5
A	EP 0 357 915 A (BAYER AG) 14 March 1990 see Table 1, examples 2,3,12 see example 1	1-5
A	EP 0 568 874 A (BAYER AG) 10 November 1993 see examples 1-6,16,17,25-27,30,32,35,36, 39	1-5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
22 January 1998	30/01/1998

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INTERNATIONAL SEARCH REPORT

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PCT/IB 97/01372

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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